TWO DIMENSIONAL SOLID STATE NMR METHODS APPLIED TO WHOLE COALS AND CHEMICALLY MODIFIED COALS

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Introduction

Carbon-13 solid state NMR spectroscopy of coals and chemically modified coals using the combination of cross polarization and magic angle spinning (CPMAS) has proven an extremely useful method for characterizing the organic structures present in these systems.[1,2] In addition to providing a direct measure of carbon aromaticity, the method gives some further indication as to the different types of organic functionalities present from the characteristic shoulders usually observed on the two principal bands in these spectra. Unfortunately it is not possible to quantitatively assign any of these features in coal CPMAS spectra to single functional types because of severe spectral overlap. For instance in the aromatic region there are typically three overlapping bands centered roughly at 127, 138 and 155ppm from TMS. As a rule of thumb the 155 band is often taken as attributable to phenols or aryl ethers, the band at 138 as alkyl substituted aromatics and the band at 127 as both protonated aromatic carbon and nonprotonated carbon in fused rings. This qualitative interpretation of CPMAS coal spectra is supported by studies using CPMAS to follow the maturation of coal.[3] As rank increases the general trend observed is that oxygenated aromatic carbons disappear first followed by loss of alkyl groups and the aromatic band becomes progressively narrower. This picture should however not be taken too literally as many other types of carbons that are to be expected in coals also resonate in these regions. The inclusion of heteroatom substitution in the unsaturates produces a wide range of carbon-13 shifts making it especially difficult to identify these important constituents of coal by solid state NMR.

These difficulties of interpretation are similar to those encountered in the study of complex biomolecules by NMR in solution. Because of the large number of resonances and the resultant spectral overlap, unambiguous assignment of the spectra is not simple. Most often in solution NMR this problem is handled by application of one of the many two dimensional (2D) NMR methods developed over the last decade.[4] In general the 2D methods used in solution are not applicable to coal because of the strong internuclear dipolar interactions present in organic solids. Our research has been concerned with the development and application of new 2D methods for solids that overcome these difficulties. We have previously reported the successful application of a version of the heteronuclear shift correlation method for solids to a whole coal.[5] This experiment permits assignment of carbon-13 resonances on the basis of the chemical shift of any directly bonded proton. In this way the protonated carbon-13 resonances in the aliphatic portion of a coal can be separated and clear distinctions made between methylenes, methyls bonded to carbon and methyls bonded to heteroatoms. In this type of experiment the idea is to produce a pulse sequence that removes the complications of the solid state to yield a result similar to the analogous experiment in solution. A much more productive approach has been to use the magnetic interactions present in solids as the basis for 2D NMR. Two such methods being studied which hold much promise for structure analysis in coals are asynchronous dipolar shift correlation spectroscopy (ADIPSHIFT) and zero field NMR

(ZFNMR).[6] These methods yield spectra with much better resolution than typically observed by CPMAS spectroscopy and provide for a more complete accounting of functional groups. Recent work in this laboratory has also indicated that 2D methods which can correlate carbon-13 resonances on the basis of connectivity are possible in solids. These methods will determine how functional groups are connected to one another and be especially applicable to chemically modified coals.

ADIPSHIFT NMR

In ADIPSHIFT NMR the resonances in a complex carbon-13 CPMAS spectrum can be separated on the basis of the number of directly bonded protons using the carbon-13/proton dipolar interaction. All types of carbon are observed in this experiment at once and it is inherently as accurate as CPMAS spectroscopy itself. This is a significant advantage over the dipolar dephasing method which cannot distinguish methines from methylenes and requires empirical corrections if semi-quantitative results are to be obtained. The experimental setup and pulse sequence used in the ADIPSHIFT experiment has been described elsewhere.[6] In brief the experiment produces a 2D spectrum with the decoupled carbon-13 CPMAS spectrum along the ω_2 axis and a proton dipolar coupled carbon-13 MAS spectrum along the ω_1 axis. To identify the types of carbon resonating at a given point in the normal carbon-13 CPMAS spectrum the dipolar sideband pattern in ω_1 for that point is simulated. The basis of the method is that a CH_2 group will give about twice as wide a sideband pattern as a CH group and both of these patterns are very much wider than those for nonprotonated carbons or rotating methyl groups. The sideband patterns are determined by a number of factors including C-H distances, H-C-H angles, chemical shift anisotropies and the relative orientation of the chemical shift anisotropy to the C-H vectors. In extensive computer simulations it has been found that under conditions of fast MAS rotation the sideband patterns are dominated by the number of protons attached. Reasonable variations in the C-H distance, chemical shift anisotropy, H-C-H angle and shift tensor orientation have only small effects on the calculated sideband intensities. Average values for relative sideband intensities can therefore be used as a basis for simulating experimental spectra. All that is necessary is to find a linear combination of the standard sideband patterns to determine the ratios of CH_2:CH:CH_3 and nonprotonated carbons contributing to a particular resonance.

In application to model systems the method gives excellent agreement with known structures. For cholesterylacetate the CPMAS spectrum is quite complex giving as many as three lines for each carbon in the molecule due to solid state effects. From the ADIPSHIFT sideband pattern for the 80-10ppm region of the spectrum the relative percentages of the three types of carbon are calculated to be 42% CH_2, 27% CH and 31% CH_3 plus nonprotonated carbons. This compares quite well with the actual numbers of 42.1%, 27.2% and 30.7% respectively. The method has also been applied to three coals: PSOC-284, PSOC-1135 and an air-oxidized Illinois#6 coal. The results from the sideband analysis for these three coals are contained in Table 1. Even though the air-oxidized coal and PSOC-284 give essentially identical CPMAS spectra, measureable differences exist in the breakdown of carbon types. The numbers in Table 1 can be used to calculate the H/C ratio for the organic portion of the coal. In each case the number is somewhat lower than that measured by analysis. For example in PSOC-284 the H/C ratio by ADIPSHIFT NMR is 0.83 and is measured by analysis to be 0.87. This difference is to be expected as the NMR measurement accounts only for hydrogen attached to carbon, that associated with heteroatoms is not accounted for.

Chemical shift spectra for the different sidebands in the ADIPSHIFT spectra also make for an interesting comparison between these coals. In the

centerband the spectra are dominated by nonprotonated and methyl carbons. The first and successive sidebands are due to CH and CH_2 groups with the latter dominating the outermost sidebands. Significant differences are observed in these coals, especially in the low field aromatic region. In the first and second sideband spectra resonances attributed to protonated sp^2 carbons are observed which are normally obscured by the resonances from phenol or phenolic ether carbons. This is a rather unique shift range for protonated carbon and is most likely attributable to carbons in furan derivatives alpha to the oxygen. Another interesting feature is a shoulder sometimes seen in CPMAS spectra of coals at ~108ppm which is now clearly resolved. These carbons are also protonated and probably are due to carbons beta to the heteroatom in phenols, furans or pyrroles. Some types of olefins will resonate in this area of the spectrum as well. In the aliphatic region the spectra clearly distinguish methyl carbons and CH_2 groups. For the poorly resolved region where ethers resonate there is now clear evidence for a substantial portion of methylenes attached to oxygen.

Zero Field NMR

While CPMAS based methods are useful for spin 1/2 nuclei such as carbon-13, they are of limited utility for nuclei with spin greater than 1/2 because of the nuclear quadrupole interaction. This same interaction is put to good use in ZFNMR which can produce exceptionally well resolved solid state spectra.[7] For coal the most important applications of ZFNMR will be to nitrogen-14 and deuterium nuclei with indirect detection via the abundant protons for sensitivity enhancement. ZFNMR of these nuclei is essentially Fourier transform pure nuclear quadrupole resonance. Because of the large variation in quadrupole coupling constants associated with changes in functionality, the ZFNMR spectra of these nuclei in coals are expected to be especially informative. ZFNMR is basically a 2D technique which correlates the high field NMR spectrum with the spectrum in zero applied field. In a typical ZFNMR experiment the zero field evolution is accomplished by removing the sample from the NMR magnet to a region in the fringe field which can then be conveniently compensated for by a set of pulsed magnet coils. The difficulty with this approach is that the relaxation times T_1 for the nuclei being observed must be longer than the time needed to move the sample out of the NMR magnet and back. Typical pneumatic shuttling times are currently 100msec which is the order of T_1 for the protons in most coals. In order to make ZFNMR applicable to coal, methods are being developed to lengthen the proton T_1's and shorten the sample shuttling times. One approach has been to remove all oxygen from the coal sample and to lower the temperature which we have found can produce T_1's as long as 800msec in coals. Another way around this problem is to not shuttle the sample and electronically switch the main magnet field instead. Switching times the order of 30msec are currently achievable with fields as large as 1.4T. This method is faster and more reproducible than pneumatic sample shuttling and much easier to combine with low temperature operation.

Connectivity by Solid State NMR

The advanced NMR methods outlined above come close to extricating all the structural information possible by NMR alone at present. Another approach to increasing the information content of NMR spectra is to combine NMR spectroscopy with chemical treatment. Some elegant work along these lines has been done using alkylation chemistry.[8,9] By incorporating a spin label in the alkylating reagent in the form of isotopic enrichment or another NMR active nucleus, the structure of the reaction site can be conveniently studied by solid state NMR methods. Previous studies have been especially informative as

to the types of sites that may be O-alkylated in coals. In particular the chemical shifts for aryl ethers are quite sensitive to sterics. This makes it possible to determine the ratio of aryl ethers formed with no substitution at adjacent carbons to those with substitution. Such chemical treatment can also be used to good advantage in 2D NMR studies. The principal piece of information that the other 2D techniques discussed here lack is connectivity, i.e., how are the functionalities observed attached to one another? The functional analysis provided by ADIPSHIFT and ZFNMR only tells us what types of carbons, protons, or nitrogen are present, not how they are linked. By using carbon-13 labeled alkylating reagents it should however be possible to establish connectivity in the area of the alkylation site using 2D NMR methods such as COSY and NOESY.[4]

The basic idea in the COSY and NOESY methods is that spin-spin couplings and internuclear dipolar couplings are short range interactions which can be used to correlate the resonances for carbons in close proximity to one another. For a number of reasons such carbon-carbon connectivity experiments may not be expected to work well in solids and this has slowed their development. One potential problem is that for pairs of carbon-13 nuclei the size of the direct dipolar coupling and the chemical shift differences may be comparable giving rise to second order effects which are observed to be pronounced in powder spectra.[10] This might be expected to give rather complicated scalar coupling patterns for bonded spins making COSY methods difficult to interpret in complex systems. In addition spin exchange mediated by direct dipolar couplings in second order systems under MAS may make it difficult to quantitate the results from NOESY type experiments and thus internuclear distances derived from such methods may not be reliable. However under MAS conditions it has been observed that these factors do not necessarily result in second order COSY or NOESY spectra and for the purposes of establishing connectivity the techniques work quite well if certain precautions are followed.

The model system studied here is the pair of phosphorus-31 nuclei in 1,2-bis[2,4,6-tri-tert-butylphenyl]diphosphine. This system was chosen for study because of the high sensitivity of phosphorus-31 NMR, the conclusions drawn are applicable to any pair of spin 1/2 nuclei with similar dipolar couplings and chemical shift anisotropies. Therefore similar behaviour is expected for pairs of carbon-13 nuclei in organic solids. In solution the phosphorus-31 spectrum displays a single line under proton decoupling for the two magnetically equivalent phosphorus nuclei. In the solid state the CPMAS spectrum is somewhat different showing two lines with barely resolved fine structure. One line has the appearence of a triplet and the second has an ill defined shape with noticeable shoulders. The nature of the fine structure has been determined to be due to ^{31}P-^{31}P scalar coupling in the solid which is not observable in solution. This was accomplished by a homonuclear J 2D experiment using CPMAS and strong proton dipolar decoupling. In addition it was found necessary to increment the t_1 period synchronously with the MAS rotation rate ω_r to ensure that the π pulse in the middle of t_1 did not interfere with the MAS process. The resultant J spectrum gives a reasonable value for J ^{31}P-^{31}P of 200Hz. The patterns in the 2D J spectrum suprisingly are observed to be very close to first order. To determine the connectivity of the transitions a COSY experiment was performed again restricting the increment in t_1 to $1/\omega_r$. The resulting 2D spectrum shows that the two lines in the ^{31}P spectrum are in fact not coupled to each other, rather they are actually two pairs of closely spaced resonances which are internally coupled. This is somewhat perplexing as the resonance which has the appearence of a triplet is seen to actually be a doublet of doublets with J close to the isotropic chemical shift difference. The reason that the pattern is not highly second order as would be observed

for this case in solution is subtle. Even though the average shift difference for these two nuclei is small, the instantaneous shift difference at many points during the MAS rotation apparently is large. This is a consequence of the fact that the two ^{31}P nuclei have anisotropic chemical shifts ($\Delta\sigma$~110ppm) and that the shift tensors are not coparallel. Thus the J spectrum and the COSY patterns are first order even though the isotropic shift difference is close to J over a MAS rotation. While this situation may seem to be fortuitous, it will in fact be the usual case in most systems of this type. Only in the case where of a pair of nuclei are related by an inversion center will scalar couplings not be observed. In carbon-13 alkylated coals it is then expected that the identification of C-alkylation sites should be possible using this solid state COSY method. All that is required is the observation of cross peaks in the 2D spectrum with the natural abundance carbon-13 at the site of attachment and these should be observed with the same sort of sensitivity as ADIPSHIFT spectra.

A second type of connectivity is also nicely demonstrated in our model system. In a typical NOESY experiment nuclei spatially close to one another are correlated via dipolar mediated cross relaxation. In the solid the experiment is conceptually similar except that the correlation is achieved directly with the dipolar couplings present rather than through relaxation processes. In the model diphosphine studied the results of the NOESY experiment are similar to those for the COSY experiment. The same first order COSY peaks are observed but now additional cross peaks are seen due to the mixing period during which the dipolar interaction correlates the resonances. This spectrum shows that although the two principal ^{31}P lines are not through bond connected, they are in close proximity to one another. Again the patterns are close to first order and of good intensity. These results lead us to conclude that there are at least two inequivalent molecules in the unit cell for this compound and that the molecules do not have inversion centers. In addition the sample used has an impurity of the analogous primary phosphine present. No cross peaks are observed between the diphosphine and the primary phosphine indicating that they are in separate phases, i.e. the two compounds crystallize out of solution separately. When applied to O-alkylated coals this method should be quite informative. Since there will be no large scalar couplings to other carbon-13 centers all cross peaks that will be observed will be NOESY peaks and indicate the identity of the carbons alpha to the oxygen or otherwise very close to the labeled center.

Summary

Two dimensional NMR methods have been shown to provide a much finer accounting of the functional types present in coals than by CPMAS spectroscopy alone. The ADIPSHIFT method has been shown to be at least as quantitative as CPMAS both in theory and experimentally. The method gives reliable distributions of carbons with differing multiplicities which is useful in identifying different functionalities that overlap in chemical shift. Recent studies of a model system indicate that the connectivity of the different groups in chemically modified coals should be obtainable from solid state COSY and NOESY experiments. This type of information will provide a very accurate picture of the structure of the alkylated sites and the substitution patterns surrounding them.

Acknowledgments

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TABLE 1

ADIPSHIFT Analysis for Three Coals

Coal	Aliphatics			Aromatics		
	$\%CH_2$, C	%CH	$\%CH_2$	%C	%CH	f_A
PSOC-284	17	39	44	62	38	0.68
Air Ox. I1. #6	22	43	35	63	37	0.69
PSOC-1135	27	48	25	70	30	0.81